Rocky Flats Environmental Technology Site· Actinide Migration Evaluation
Meetings January 10-11, 2000
Advisory Group
Greg Choppin, David Clark, David Janecky, Leonard Lane, Kirk Nordstrom

Summary and recommendations for path forward

We see great value in the integration of projects and are pleased with the present evolution of efforts Simultaneously, we see a need to increase AME activities focused on the industrial area, as this is essential for meeting the 2006 targets Contributing to this integration of projects and increase in focus on the industrial area, we are looking forward to the reports on the water balance work and periodic updates on the pathway analysis report

In communicating results, we have observed that oversimplification of AME findings has resulted and can continue to result in misleading statements In particular, we recommend that standard chemistry text definitions be used in presenting and discussing solubility (e g Pu referred to as relatively insoluble and uranium referred to as slightly soluble)

Progress and integration

The recent integration between D&D and AME activities is very valuable and provides an excellent example of work that utilizes detailed scientific measurements to resolve a near-term applied problem

In view of their direct connection at RFETS, the Group recognizes the benefits of continued coordination of Site activities in monitoring and modeling groundwater and surface water flow, and transport processes Further coordination and use of common or integrated data sets between water and wind erosion modeling activities will be valuable

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Results and Discussions

Uranium Speciation Modeling – Jim Ball

The geochemical speciation modeling for uranium has added some important details to the understanding of the Solar Ponds Plume, while pointing out some additional analytes that could contribute to our understanding of groundwater and plume processes Identification of the correspondence of high uranium concentrations with large anion charge imbalances suggests that analyses of common organic ligands (e g citrate, oxalate and EDTA) from samples within the plume would be valuable Comparing maps of the Solar Ponds Plume area with charge imbalance, nitrate, uranium and organic ligand data would likely improve our understanding of the correspondence between the uranium plume as drawn on maps and the nitrate plume – especially in the area(s) where the uranium plume has been drawn outside the nitrate plume

A very interesting conclusion is the calculation of undersaturation of uranium minerals in all the samples, suggesting control by sorption This result has potentially important implications with respect to the quantity of uranium introduced by the plume In completing the speciation modeling study, comparison of the results of these calculations with uranium solubility at other sites will be valuable It is important to confirm that the thermodynamic database is not biased and that these solutions are definitely undersaturated with uranium minerals Other uncertainties need to be examined as well For example, what is the sensitivity of these calculations to temperature, industrial organic ligands, measurement uncertainties?

In view of their direct connection at RFETS, there are great benefits in continued coordination of Site monitoring of groundwater and surface water, with the modeling of groundwater geochemistry and evaluating transport processes For example, integration between the water composition measurements, and the investigation of organic anion concentrations should be closely coupled with uranium isotopic analyses within the solar ponds plume system, water balance investigations and historical records of the process

Conceptual Model Document

Many of the Conceptual Model comments provided by the Technical Review Group (TRG), of the Citizen's Advisory Board, were very reasonable and will be of great help in revising the Conceptual Model document The TRG comments can be divided into three recommendations (i) justification and need for references, (ii) clarification, and (iii) further model coverage The first two recommendations are that the document be clarified and citations of references be included to back up statements in the document These are both reasonable and desirable, and will be relatively easy to provide We thank the TRG for bringing this to our attention

However, from the nature of many of the more detailed comments on further model coverage, and the recommendation for expansion of the model, the purpose of the Conceptual Model was apparently not very clear In particular, the Conceptual Model is not intended to be a detailed model of actinide migration at the Site Instead, the Conceptual Model was developed to guide and focus the dialogue among the Site, the AME group, regulators and the public, and as a "conceptual" model to help guide our thinking and discussions In addition, the document serves as an aid to ensure that the potential actinide migration pathways are not overlooked As a result, comments that the model is "too simplistic" or that it "should be expanded" are really not appropriate, because the model is supposed to be *conceptual* only We reiterate that *it is not intended to be a detailed model of actinide migration at the Site* Through use of the model to guide discussions and thinking, many new studies have appeared in the yearly workscopes of the Site The varied site reports on this research is where detailed discussion and references requested by the TRG can be readily found, and references to these reports will be added to updates to the Conceptual Model document

Finally, many of the detailed comments requested by the TRG will in fact, become available in a single document this year in the form of the Pathway Analysis Report This report was always intended to be the primary tool by which this detailed information would be summarized and made available

Water Balance

The AME Advisory Group made recommendations in the Oct 21-22, 1998 meeting notes (p 5-6) that a water budget (also called a water balance) was needed for RFETS The area for the water budget should include the Industrial Area, the SPP, and the 903 Pad areas inclusive of Walnut Creek and Woman Creek watersheds The water budget is the foundation for understanding water transport processes andimplementing transport modeling At the time of this meeting, a water budget contract is being processed by RFETS

As D&D continues for buildings and process lines in the Industrial Area, the water budget will be affected Such changes could impact the rates and directions of contaminant flows, and thus need to be determined Water transport between groundwater and surface water need to be understood well enough so that remediation can proceed without sudden, unanticipated contaminant releases to surface waters The water budget and its changing status over time must be integrated with other models and regulatory requirements that focus on contaminant transport by water flow

GS10 Water Quality and Air Sampling Data Discussion

Bob Nininger presented an update on water quality monitoring and air sampling data In particular, he focused on the data that is being collected at GS10 and in its subdrainages Integration of water quality and air quality efforts through these efforts is a significant improvement of the site program and impact on closure decisions and communication

Progress has been made toward understanding exceedances at GS10 We will be interested in the results and options pursued for further sampling of surface waters, groundwaters, soils and/or remote measurements (e g HPGe) Further questions include What is the relative priority for subsidiary samplers to

GS10? How will these efforts be integrated with the erosion modeling activities? This is very valuable in characterizing the source of elevated Am contaminants and potential for D&D impacts Continued coordination and development of common data sets will strengthen interactions

Presentation of Erosion, Sediment Transport & Pu Transport Modeling -- Win Chromec, Greg Wetherbee, Ken Spitze, and Jeff Meyers.

The USDA Water Erosion Prediction Project (WEPP) hillslope model was parameterized to local RFETS conditions This entailed describing the long term climatic features and weather statistics, quantifying hillslope descriptive features such as soil texture, slope lengths and gradients or steepness, rangeland plant growth parameters, and the required land use and management information As the WEPP model is a continuous simulation model, these input data are then used to simulate daily weather inputs, daily water balance, and plant growth In addition to these "measureable" model inputs and parameter values, the model requires some "derived" parameter input values (e g saturated hydraulic conductivity, interrill (raindrop impact and sheet overland flow) soil erodibility, rill (concentrated flow paths) erodibility, and critical shear stress which the concentrated flow must exceed to detach soil particles)

Application and calibration of the WEPP model to RFETS conditions consisted of specifying/estimating the measurable inputs and obtaining the derived parameter values by calibration Calibration consisted of varying the derived parameter values, over a permissible range of values, to most closely match observed runoff and sediment yield as measured at the hydrologic monitoring stations Rainfall simulator data collected south of the RRETS in June 1999 were also used in the calibration

Procedures, difficulties, and results of calibrating the WEPP model to the rainfall simulator runoff and sediment yield data and to gauging station runoff and sediment concentration data from the monitoring network were described Historically, the WEPP model has been tested and evaluated using rainfall simulator data from rainfall simulator plots of varying width and a standardized length of 10 7 m Extending a simulation model evaluated and parameterized using data from 10 7 m long plots to hillslopes at RFETS of up to several hundred meters in length represents an extreme extension in the scale of application for the WEPP model

Comparisons between WEPP calibration results and measured results for a limited number of gauging sites on RFETS were presented Overall, the WEPP model seemed to represent the observed gauging station data fairly well although no goodness-of-fit statistics were presented

A geographic information system (GIS) was used to describe the detailed topography of the hillslopes draining from the 903 Pad area to the South Interceptor Ditch (SID) The GIS was also used to convert WEPP erosion/sediment yield estimates at one hundred points within each overland flow element (OFE) used to represent the hillslope These closely spaced data points were then used to prepare detailed color maps illustrating areas of soil erosion and sediment deposition Next, Pu concentration data from soil sampling sites in the 903 Pad and hillslope areas contributing to the SID were subjected to geostatistical analyses and kriging techniques were used to estimate Pu concentrations at each of the 100 soil erosion/deposition estimation points in the OFE's Finally, GIS techniques were then used with the WEPP modeling results to estimate Pu concentration in eroded, transported, and deposited sediment along the hillslopes contributing to the SID Color maps describing the distribution of Pu contamination from the 903 Pad Area to the SID were then prepared to illustrate the application of the WEPP model, kriging, and GIS technology to estimate Pu source, transport and fate

These preliminary results were encouraging as a way of integrating advanced erosion modeling, geostatistical analyses, and GIS techniques to estimate Pu transport processes at RFETS

Suggestions for Erosion and Contaminant Transport Modeling Path Forward:

- DQO's should be included in the forthcoming report and should be separated into two groups of model inputs those which are "measurable" and those which are "derived" A key distinction the Group wishes to make is that "derived" parameters may be varied or modified in the calibration process whereas the "measurable" ones are estimated and then left fixed throughout the simulations
- The insitu and detached sediment particle size distributions used in the erosion and sediment transport calculations need to be explicitly identified, discussed and related to other Site studies of particle size distributions and soil aggregation processes and measurements (e g Santschi and Granville)
- The Group also recommends a discussion of the scale, grid size, and delta x used in the kriging, GIS, and modeling activities and how they are related The gist of the recommendation is that in the report, authors should try to identify error propgations and smoothing as a result of the scale of discretization used in each phase of the contaminant transport calculations

Comments, Recommendations, and Concerns- Sediment and Contaminant Modeling in Stream Channels at RFETS. The AME group has commented on the WEPP modeling efforts and expressed our concerns related to expression of uncertainty in the model predictions, especially with respect to scale in extending WEPP to the long hillslopes at RFETS We also would recommend further written discussion of the results of calibration and a compilation of all measured and fitted data used in the model-gaging station data comparisons, and some statements as to the goodness-of-fit of calibrated vs observed data We understand that WEPP represents the hillslope phase of soil erosion and sedimentation and that if significant sediment deposition occurs in the stream channel systems above the streamflow gaging sites that the WEPP model might overpredict sediment yields and concentrations at these points

The AME Advisory Group also recognizes that, relative to the amount of professional activity devoted to WEPP, less attention has been devoted to the water and sediment routing in stream channels The use of the HEC6T model for stream channel routing at RFETS is an important advance and the Group recommends additional sensitivity and uncertainty analyses devoted to the channel routing problem vis a vis HEC6T and the planned channel sediment sampling procedures In parallel to the WEPP approach, we also recommend that the inputs required to HEC6T be separated into two categories "measurable" and "derived"

In summary, this work is a major contributing driver for integrated evaluation of the interaction of natural transport processes with contamination at Rocky Flats It requires the development of coordination and common data sets that will benefit closure decisions and operational responses

Soil Aggregation Experiments – Jim Ranville

Jim summarized his recent results on the distribution of Pu in soils as affected by soil aggregation He showed Pu distributions among particle sizes from <10K Daltons (molecular weight units) to 2000 micrometers as a function of different disaggregation procedures One of the most striking results is the change in the Pu distribution when the soil is desegregated by hydrogen peroxide Peroxide effectively oxidizes organic matter and the pronounced shift in Pu to smaller particle sizes (colloidal size) suggests that natural organics are important in the binding of Pu as a component of aggregated soils and that soil aggregation is strongly affected by organic matter Hence, the amount and type of organic matter may have a major influence on the mobility of Pu colloids and that undisturbed grasslands should minimize Pu mobility Conversely, processes that breakdown organic matter and disaggregate soils would tend to increase mobility, at least locally Certainly, periods and locations of high runoff and high mechanical erosion would release small particles with the potential to cause high local Pu mobility Jim speculated that fires may destroy organics and cause respirable size fractions carrying Pu to form, but further work is needed to determine whether this is a plausible hypothesis and a significant contributor to mobility

Concrete Leaching and D&D Operations

Pat Ervin presented an overview of the issues, drivers and options for D&D of the site buildings and their contaminated components In addition to plutonium and americium contamination, uranium is a recognized issue due to its presence as both a background and anthropogenic component in concrete building materials The collection of samples for measurements this year of Pu oxidation and structural state in contaminated building materials will provide the best possible understanding of the character of contamination A better understanding of information available in this area from other sites would be valuable, including data from the K-25 plant at Oak Ridge, the BNFL Sellafield gaseous diffusion plant, and Uranium Mill Tailings projects The AME Advisory Group hopes to continue to be briefed on these issues and decisions so that it can encourage and facilitate integration

Presentation to Kaiser Hill Senior Management.

The AME group met with Bob Card, Dave Shelton, John Rampe and Joe LeGare to provide an update on the goals, results, and future products of the AME The discussion that resulted included

- The role and use of the Conceptual Model to encourage public involvement
- The association of Pu in surface water solids with small (< 2 micron) particles and the kinetics of settling in the water column
- The conclusion that physical (particulate transport) is the dominant mechanism for plutonium migration at RFETS, and the recognition of a need for development of an erosion model
- The conclusion that the chemical form of plutonium at the 903 Pad is insoluble PuO_2, and the assessment that plutonium from other sources will likely be insoluble forms as well, leads to the conclusion that soluble plutonium transport models (RESRAD) are not relevant to the site
- Preliminary results from the erosion model were discussed, and everyone was encouraged by its potential to model the impact of potential barriers to erosion in future scenarios

The AME group was asked to begin thinking about how to use the results of the AME investigations to assist in 1) integrating D&D and ER activities, 2) developing future remediation strategies, and 3) protecting surface water quality

Proposal for DOE Environmental Management Meeting

Actinide characterization and migration studies at RFETS have often been at the forefront of such studies at DOE weapons complex facilities undergoing decommissioning and closure Positive identification of the form and oxidation state of plutonium in soils, recognition of the importance of insoluble but colloidal Pu transport processes, quantification of erosional transport at the Site, determination of the relative importance of air transport vs water transport, and identification of the impact of natural background uranium levels on site remediation are some of the AME studies that directly tie into site cleanup The success of these and similar studies at other weapons facility sites, along with the need for closure a few years ahead, suggest that the year 2000 would be an appropriate time to organize a national meeting among investigators, remediation teams, D&D teams, and regulators from DOE weapons complex sites This meeting would provide an opportunity to discuss the variety of approaches to remediation of actinide contamination, conceptual model formulation and how it relates to remediation, and unanticipated problems with actinide migration and experience gained with real site data Such a meeting would be of tremendous value to DOE, and could demonstrate the leadership of the Kaiser-Hill team

Pu Most Probable Chemical Forms and Transport at RFETS

Soils: The probability of release of plutonium from RFETS soils to the surrounding environment is related to a variety of factors, some of which are

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currently being addressed by Actinide Migration Evaluation The fate and transport of plutonium is governed by the solubility of its compounds in groundwater and surface waters, the tendency of plutonium compounds to be adsorbed onto mineral phases in soil particles, and by the process that cause the colloidal forms of plutonium to be filtered by the soil or rock matrices, or to aggregate, adsorb and settle during transport

The solubility of plutonium compounds depends largely on the oxidation states, and, secondarily, on the relative crystallinity of the compounds As in the case of other polyvalent metal cations, the lower oxidation states of plutonium are more stable in acid solution, and the higher oxidation states are more stable in basic solution Complexation can alter these generalizations For example, the greater hydrolysis of Pu(IV causes Pu(V,VI) to be reduced to Pu(IV) in neutral media In addition, the compounds of plutonium can contain multiple oxidation states, even though we conventionally describe them by their dominant oxidation state (e g PuO_2 and $Pu(OH)_4$)

Generally, dissolved plutonium will exist in aqueous solution as Pu(V) and Pu(VI), with Pu(V) predominating in oxidized waters For plutonium in the lower oxidation states (III) and (IV), the solubilities are exceedingly low Oxidation or reduction of higher oxidation states can lead to the formation of colloidal forms of "$Pu(OH)_4$" or "PuO_2 $2H_2O$" often referred to as "plutonium hydrous oxide" or "Pu(IV) polymer" Pu(IV) colloids are kinetically stable in solution, and eventually tend to be absorbed and/or filtered due to interactions with mineral and soil phases The slow recrystallization of Pu(IV) colloids leads to greater stability and lower solubility

In natural waters plutonium solubility is limited by the formation of compounds that range from amorphous $Pu(OH)_4$ to polycrystalline PuO_2 A reasonable estimate for the solubility of $Pu(OH)_4$(am) is $10^{-9(\pm 2)}$ M, while the solubility of PuO_2(c) is $10^{-15(\pm 3)}$ M This estimate puts an upper limit on the amount of Pu that can be present, even if Pu(V) or Pu(VI) are the more stable solution forms Pu(V) has a low tendency to hydrolyze and form complexes with ligands, and is much less likely to be sorbed to solid surfaces and colloidal particles than the other oxidation states of plutonium As a result, plutonium can be expected to migrate most rapidly as a dissolved species if it is in the pentavalent oxidation state The total solubility however, remains limited by the formation of the highly insoluble amorphous $Pu(OH)_4$ Sorption of hydrolyzed Pu(IV) in natural water on mineral surfaces and surfaces coated with organic material is accountable for the very low concentrations of dissolved Pu even in the absence of $Pu(OH)_4$(am) or PuO_2 (c) The strong tendency of $Pu(OH)_4$ to sorb on surfaces is a dominant and often controlling feature in plutonium geochemistry

The data amassed during AME studies is consistent with the above expectations of plutonium chemistry The data indicate that plutonium in RFETS surface waters has an extremely low solubility, with concentrations of "soluble" plutonium in the femtomolar (10^{-15} M) range, similar to global fallout This extremely small amount of "soluble" plutonium (at femtomolar concentrations) is consistent with plutonium(V) The data also indicate that the bulk of plutonium is associated with colloidal particles, consistent with plutonium(IV) chemical behavior Extended X-ray Absorption Fine Structure (EXAFS) studies show that plutonium in soils taken from the 903 Pad is plutonium(IV), and in the chemical form of relatively insoluble PuO_2 This is significant in that it had been widely held at the Site that the chemical form was the dioxide, but this had never been proven The synchrotron radiation studies unequivocally demonstrate that it is indeed PuO_2

Concrete and process waste lines: The source of the plutonium contamination in concrete varies, but can be categorized as either resulting from fires (smoke), or resulting from nitric acid spills inside the buildings It is likely that any plutonium contamination deposited from fires would be the oxide, PuO_2 In nitric acid process chemical solutions, high acid concentrations are used to prepare $Pu(NO_3)_6^{2-}$ which was used for anion exchange purification The high acid concentration prevents Pu(IV) hydrolysis Since concrete is highly basic, and plutonium, particularly Pu(IV) is exceedingly susceptible to hydrolysis and polymerization reactions As a result, neutralization of a nitric acid solution of Pu(IV) will result in almost immediate generation of the hydrous oxide (or intrinsic colloid) of Pu(IV), often described as $PuO_2{\bullet}2H_2O$ This is also the anticipated result for a nitric acid solution of Pu(IV) being spilled onto soil, where it will ultimately become neutralized and hydrolyze Subsequent aging of hydrous oxide will lead to loss of water and recrystalization These hypotheses will be tested this year using synchrotron radiation studies on concrete samples

The role of aqueous transport calculations at the RFETS: Since we anticipate that the chemical form of plutonium in either the soils or concrete will be relatively insoluble, transport-modeling calculations that assume soluble forms of plutonium are likely to be of little value Indeed, while we point out that plutonium in soils at RFETS is relatively insoluble, uranium on the other hand can be classified as being slightly soluble Therefore, uranium will pose a higher probability of aqueous dissolved transport A thorough understanding of the uranium geochemistry, the uranium source-term, and the overall water balance at the Site are therefore of greater importance with respect to transport calculations

At the public meeting, questions were raised about Kersting et al's publication on migration of Pu in groundwater at the NTS We point out that the maximum measured concentration of Pu at the ER-20-5 site at NTS was approximately 10^{-14}M (a value within fallout levels) This value is lower than the solubility measured for Pu(V) compounds, and is within the solubility range measured for of PuO_2 of $10^{-12} - 10^{-17}$M The NTS studies indicate that >99% of the Pu was associated with colloidal particles, though it was not determined whether the Pu was intrinsic radiocolloid, or whether the Pu was associated with colloidal sized clay and zeolite particles in the groundwater The point of the paper was to point out that transport models that don't include colloid-facilitated transport (i e particulate transport) may inaccurately predict the migration of plutonium

So, what is the similarity to RFETS? First, is has been independently recognized (prior to the Nature publication) that particulate transport is not only important, but likely to be the dominant migration pathway for plutonium for RFETS soils and waters Further, at NTS, large amounts of plutonium were "injected" 300 meters below the surface by the nuclear detonation Based on experience at RFETS and elsewhere, plutonium dispersed by the detonation forms oxide compounds associated with the rocks and colloids From drill-back operations, we know that approximately 98% of the plutonium is present in the melt-glass that forms in the bottom of the cavity These melt glasses are extremely radioactive and glasses are less stable than crystalline materials We also know that extremely high radiation fields will damage the glass (over short time periods), and could conceivably result in the formation of a variety of materials, including additional small silicate colloids with associated plutonium The situation at RFETS is very different from the NTS The plutonium particles are confined to surface soils and disturbed ground (e g building footings, drains, trenches, and infrastructure) Furthermore, we do not have the extremely high radiation fields associated with plutonium particles dispersed in the soils at RFETS, and the plutonium is not encased in silicate glass but is in the form of plutonium compounds (e g PuO_2) So the primary similarity is the confirmation that one must include particulate transport in migration models

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Documents provided to advisory group

Geochemical Modeling of Solar Ponds Plume Groundwater at the Rocky Flats Environmental Technology Site, viewgraphs from Jim Ball, USGS

Geochemical Modeling of Solar Ponds Plume Groundwater at the Rocky Flats Environmental Technology Site Part I Ion Plots and Speciation Modeling, report by J W Ball, USGS

TRG Comments on the Conceptual Model for Actinide Migration Studies at the Rocky Flats Environmental Site – summary, Technical Review Group comments, and comments from contractors Hakonson, Whicker, Higley

HEC-6T Sediment / Actinide Transport Model Development, notes and figures from Greg Wetherbee, WWE

Erosion/Surface Water Modeling Development and Results, notes and figures from Win Chromec, RMRS

Actinide migration evaluation for the Rocky Flats Environmental Technology Site Fiscal Year 2000 Activities – December 14, 1999, from Chris Dayton, Kaiser-Hill

Status of Actinide Migration Evaluation Projects, January 10, 2000, listing passed out at public meeting by Chris Dayton, Kaiser-Hill

The Influence of Soil Aggregation on Pu Distribution in Rocky Flats Buffer Zone Soils, viewgraphs from James Ranville, CSM

Actinide Migration from Concrete, viewgraphs from Pat Ervin and Jeff Stevens, Kaiser-Hill

Actinide Migration Evaluation at Rocky Flats Environmental Technology Site, viewgraphs

Documents and information requested for advisory group

Process waste line maps – new lines and old lines

Preliminary kriging maps and image analysis derivative map of Pu/Am ratio

Pu and Am surface water monitoring data in electronic spreadsheet format since October1997 (Pu & Am concentration and uncertainties, locations and dates)

'1/10/00 puam2hr xls' file for WEPP/HEC-6TS Simulated total actinide activity for the 2-year, 2-hour rainstorm (31 5mm) plot with added Pu/Am ratio

Participants in AMS technical meetings

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